

Synthesis, Structure, Optical Properties and Theoretical Studies of $\text{Pt}(\text{P}-\text{P})(\text{CN})_2$ with $\text{P}-\text{P} = 1,2\text{-Bis}(\text{diphenylphosphanyl})\text{benzene}$ and $2,2'\text{-Bis}(\text{diphenylphosphanyl})\text{-1,1'-binaphthyl}$ – Luminescence from Metal-to-Ligand Charge Transfer and Intraligand States

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The complexes $\text{Pt}^{\text{II}}(\text{P}-\text{P})(\text{CN})_2$ with $\text{P}-\text{P} = 1,2\text{-bis}(\text{diphenylphosphanyl})\text{benzene}$ (dppb) and $2,2'\text{-bis}(\text{diphenylphosphanyl})\text{-1,1'-binaphthyl}$ (binap) were synthesised and characterised by elemental analysis, ESI MS and electronic spectroscopy. The structure of $\text{Pt}(\text{dppb})(\text{CN})_2$ was resolved by single-crystal X-ray diffraction. This compound consists of mononuclear Pt^{II} complexes with an almost planar PtP_2C_2 coordination. While both complexes are not luminescent in solution, they show an emission in the solid state under ambient conditions. It is suggested that the luminescence of $\text{Pt}(\text{dppb})(\text{CN})_2$ originates from a ($\text{Pt}^{\text{II}} \rightarrow \text{dppb}$) metal-to-ligand charge transfer (MLCT) triplet with some dppb intraligand (IL) contribution. This assignment is confirmed by calculations

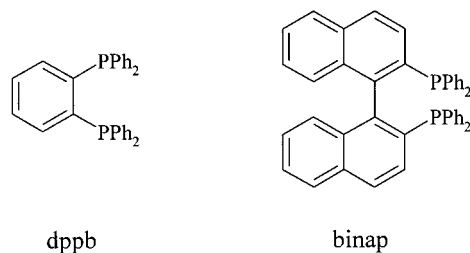
which provide further insight into the excited state properties of the complex. In solution the phosphorescence is absent because the MLCT/IL state is deactivated to a non-emissive ligand field (LF) triplet, which is located at rather low energies owing to its distortion towards a tetrahedral structure. In the solid state this distortion is hindered. In the case of solid $\text{Pt}(\text{binap})(\text{CN})_2$, the phosphorescence is apparently of the IL type as the $\pi\pi^*$ triplet of the binaphthyl chromophore occurs at low energies. Again, in solution the phosphorescence is absent owing to the interference by a distorted LF state.

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1. Introduction

A variety of square-planar Pt^{II} complexes has been shown to be luminescent under ambient conditions.^[1–3] Diverse potential applications have stimulated interest in these compounds.^[3] Generally, mononuclear Pt^{II} complexes emit from their lowest-energy triplet, which may be of the metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT) or intraligand (IL) type. Pt^{II} complexes with low-energy ligand field (LF) triplets are not emissive at room temperature. The complex $\text{Pt}(1,2\text{-diimine})(\text{CN})_2$ with 1,2-diimine = 4,7-diphenyl-1,10-phenanthroline is a typical example of a Pt^{II} complex which emits from an IL triplet.^[4] This room temperature phosphorescence is facilitated by the low energy of the $\pi\pi^*$ diimine IL states as well as by the strong LF strength of the cyanide ligands which push interfering LF states to rather high energies.^[4] The number of emissive Pt^{II} complexes may be increased considerably if the diimines of $\text{Pt}(1,2\text{-diimine})(\text{CN})_2$ are re-

placed by other strong-field ligands with low-energy excited states. Promising candidates are bidentate phosphanes that carry aromatic chromophores. We explored this possibility and selected the complex $\text{Pt}^{\text{II}}(\text{P}-\text{P})(\text{CN})_2$ with $\text{P}-\text{P} = 1,2\text{-bis}(\text{diphenylphosphanyl})\text{benzene}$ (dppb) and $2,2'\text{-bis}(\text{diphenylphosphanyl})\text{-1,1'-binaphthyl}$ (binap) for the present study (Scheme 1).



Scheme 1

The aromatic chromophores of these ligands were expected to serve as luminophores^[5] of both complexes. In this context it should be mentioned that a few Pt^{II} phosphane complexes have been reported to display luminescence. However, these emissions do not originate from IL states. In some cases the phosphanes are only spectator

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ligands and are not directly involved in emission.^[6–8] In other cases the luminescence is associated with metal–metal interactions in binuclear Pt^{II} complexes.^[9,10] Our target compounds Pt(P–P)(CN)₂ were expected to be accessible by simple synthetic procedures.

2. Results and Discussion

Experimental Results

The complexes Pt(dppb)(CN)₂ and Pt(binap)(CN)₂ were obtained as white or slightly yellow solids by the reaction of Pt(CN)₂ with dppb and binap, respectively. The composition was confirmed by elemental analysis and mass spectroscopy. The positive ion electrospray mass spectrum (+ESI MS) of [Pt(dppb)(CN)₂] in CH₃CN (+ 1% CH₃COOH) consists of peaks at *m/z* = 693, 694, 695, 696 and 697. The complex has apparently added one proton at the cyanide ligands. In addition, peaks at 1358, 1359, 1360, 1361, 1362, 1363 and 1364 indicate the presence of the dimer Pt₂(dppb)₂(CN)₄ which has lost one cyanide ligand. The +ESI MS spectrum of the binap complex shows an analogous pattern. The complex Pt(binap)(CN)₂ in its monoprotonated form displays peaks at 869, 870, 871, 872 and 873, while peaks of the cation [Pt₂(binap)₂(CN)₄]⁺ appear at 1710, 1711, 1712, 1713, 1714, 1715, 1716 and 1717. In all cases there is a good agreement between the calculated and observed isotopic peak pattern.

The electronic spectrum of dppb in CH₃CN/CH₂Cl₂ (1:1) exhibits an absorption at $\lambda_{\text{max}} = 276 \text{ nm}$ ($\epsilon = 17\,920 \text{ M}^{-1} \text{ cm}^{-1}$). At room temperature, solutions of dppb are not emissive, but in ethanol glasses at 77 K a strong phosphorescence appears at $\lambda_{\text{max}} = 502 \text{ nm}$. The absorption spectrum of Pt(dppb)(CN)₂ in CH₃CN (Figure 1) shows bands at $\lambda_{\text{max}} = 295$ (1420), 267 (12 940) and 225 nm (sh, 51 570). Solutions of the complex do not emit. However, at room temperature the solid compound shows a slightly structured luminescence (Figure 1) at $\lambda_{\text{max}} = 502 \text{ nm}$ with shoulders at approximately 480 and 540 nm. The absorption spectrum

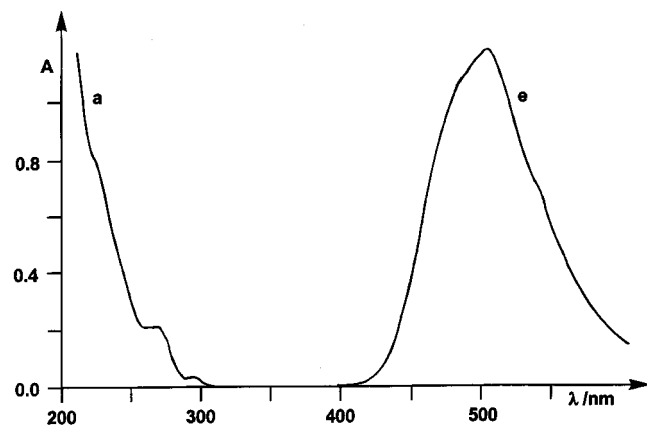


Figure 1. Electronic absorption (a) and emission (e) spectrum of Pt(dppb)(CN)₂ at room temperature; absorption: $1.54 \times 10^{-5} \text{ M}$ in CH₃CN, 1-cm cell; emission: solid, $\lambda_{\text{exc}} = 300 \text{ nm}$, intensity in arbitrary units

of Pt(binap)(CN)₂ in CH₃CN (Figure 2) contains bands at $\lambda_{\text{max}} = 343$ (3500) and shoulders at about 314 (5100), 290 (8500), 262 (33 500) and 220 nm (86 000). Again, in solution the complex does not emit, but the solid compound exhibits a luminescence at $\lambda_{\text{max}} = 513 \text{ nm}$ with distinct structural features at 470, 550, 600 and 640 nm (Figure 2).

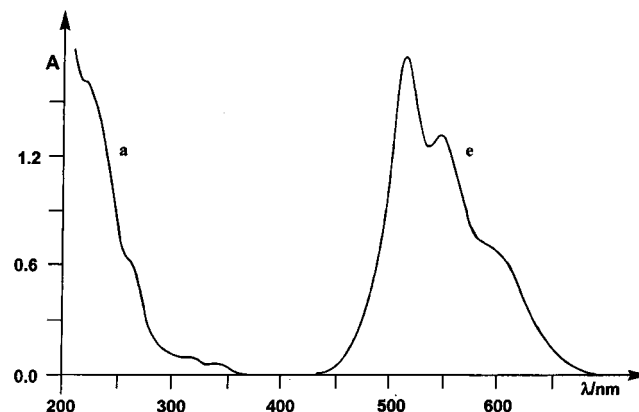
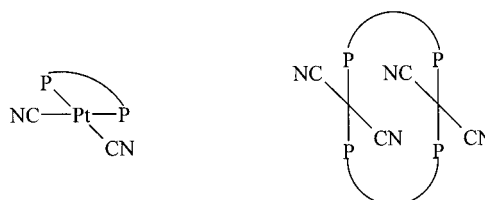


Figure 2. Electronic absorption (a) and emission (e) spectrum of Pt(binap)(CN)₂ at room temperature; absorption: $2.06 \times 10^{-5} \text{ M}$ in CH₃CN, 1-cm cell; emission: solid, $\lambda_{\text{exc}} = 350 \text{ nm}$, intensity in arbitrary units

Interpretation

Complexes with the general composition Pt^{II}(P–P)(CN)₂ may be monomeric or dimeric^[9,10] (Scheme 2).



Scheme 2

In the dimers the cyanide ligands occupy *trans* positions and both square-planar Pt^{II} complex moieties are connected by bridging phosphanes. With regard to the complexes Pt(dppb)(CN)₂ and Pt(binap)(CN)₂, our analytical data do not provide an unambiguous distinction. The MS spectra indicate the presence of monomers as well as dimers. However, the dimers Pt₂(P–P)₂(CN)₄ with P–P = bis(diphenylphosphanyl)methane, bis(dimethylphosphanyl)methane and bis(dicyclohexylphosphanyl)methane show an intense absorption ($\epsilon > 10^4$) around 330 nm, which is associated with the Pt–Pt interaction.^[9,10] These absorptions do not appear in the spectra of Pt(dppb)(CN)₂ and Pt(binap)(CN)₂. Accordingly, the latter complexes are either monomeric at least in solution, or dimeric but with large Pt–Pt distances that prevent any efficient metal–metal interaction.

For Pt(dppb)(CN)₂, the monomeric structure was confirmed by single-crystal X-ray diffraction (Figure 3). The complex is essentially planar with P–Pt–P and C–Pt–C bond angles of 86.6° and 89.3°, respectively. The average

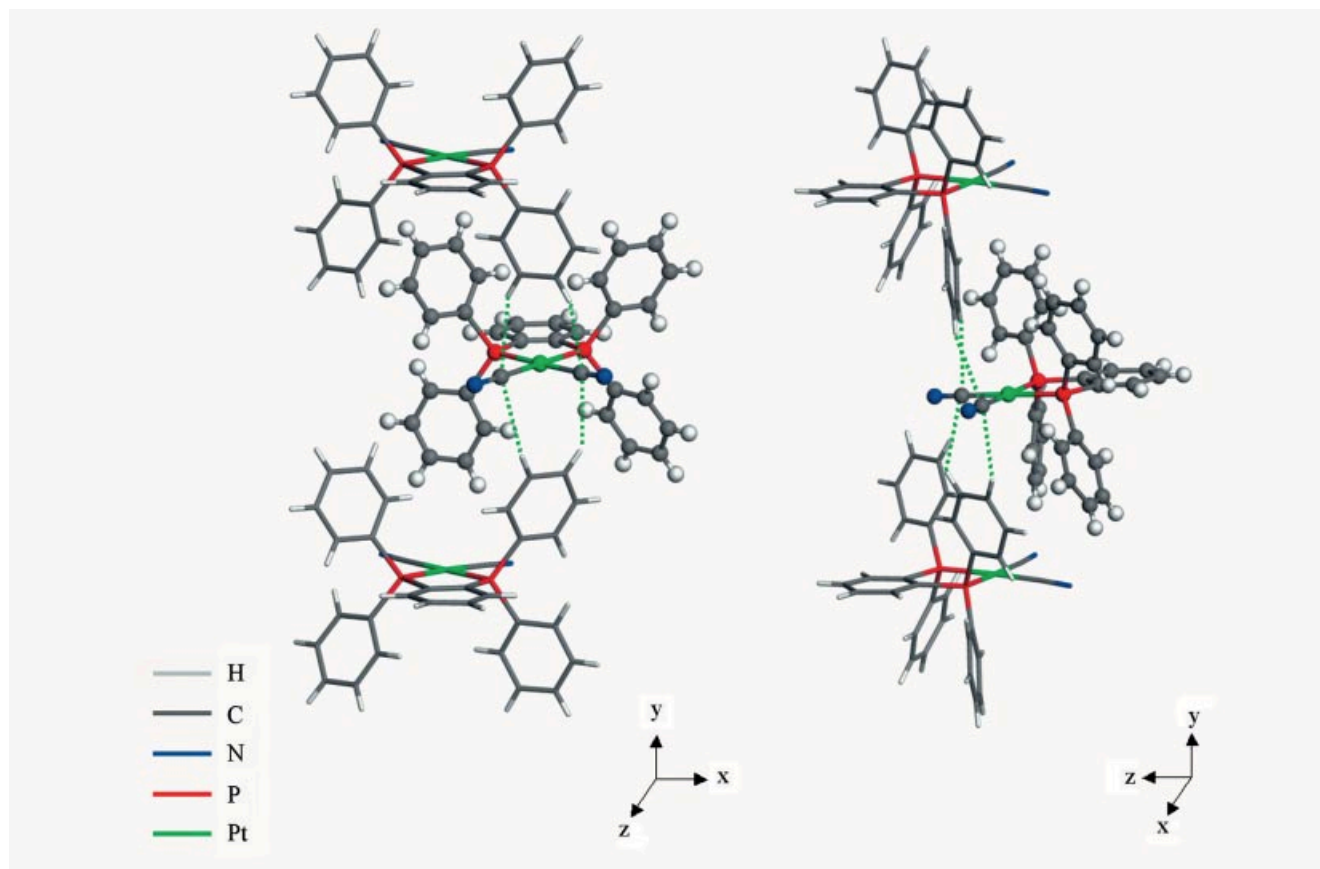


Figure 3. Crystal structure of monomeric $\text{Pt}(\text{dppb})(\text{CN})_2$: visualisation of the steric interactions between the $\text{Pt}(\text{CN})_2$ fragment and two phenyl groups from neighbouring molecules

metal–ligand bond lengths are 2.26 Å for Pt–P and 1.98 Å for Pt–C. Cyanide is coordinated in a linear fashion.

The lowest-energy excited state of $\text{Pt}(\text{dppb})(\text{CN})_2$ seems to be of the IL type since the complex and the free ligand show this phosphorescence at the same wavelength ($\lambda_{\text{max}} = 502 \text{ nm}$). However, the lowest-energy transitions of simple aromatic phosphanes are associated with the promotion of an electron from the lone pair (l) at the phosphorus atom to the π^* orbitals of the aromatic substituents.^[11] Upon coordination the lone pair is stabilised by σ -bonding. As a consequence, the $l \rightarrow \pi^*$ transition of the phosphane becomes a $\sigma \rightarrow \pi^*$ IL transition that should be shifted to higher energies.^[11] This concept does not seem to apply to dppb and $\text{Pt}(\text{dppb})(\text{CN})_2$. Fortunately, theory provides a satisfactory explanation. According to density functional calculations, the emitting state of the complex is a MLCT state that contains a $\sigma \rightarrow \pi^*$ IL contribution. The HOMO is essentially metal-based but also includes the Pt–P bonds, while the LUMO is largely restricted to the aromatic substituents (Figure 4).

To get further insight into the electronic structure and geometry of the excited state of the $\text{Pt}(\text{dppb})(\text{CN})_2$ molecule, additional density functional calculations were performed. Optimising the geometries of the singlet-ground state (S_0) and the first triplet state (T_1) results in a quadratic-planar coordination geometry with respect to Pt^{II} for

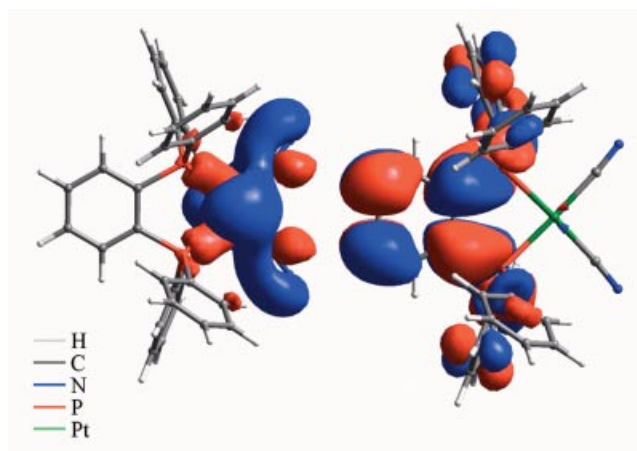
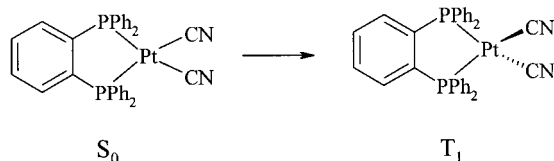


Figure 4. Frontier orbitals of the electronic transition at planar geometry: HOMO (left) and LUMO (right)

the ground state, while the geometry is heavily distorted in the triplet state yielding a deformed tetrahedral geometry as indicated in Scheme 3.

The angle between the cyanocarbons and Pt amounts to 160° , thus resembling more a linear coordination geometry regarding platinum and the two cyano groups than a true tetrahedron. Due to this distortion, the calculated energy gap between the triplet state and the ground state is reduced



Scheme 3

to 0.1 eV at the triplet geometry. Therefore energetic relaxation of the triplet state should be dominated by nonradiative vibrational relaxation, thereby explaining the nonemissive behaviour of the molecule in solution.

To understand the origin of this distortion an orbital correlation diagram was derived from the density functional calculations. A schematic version is shown in Figure 5. Starting on the left the excitation process promotes one electron from the HOMO to the LUMO and generates the S_1 -state. The character of this transition is best described as MLCT, which can be seen in Figure 4, where the frontier orbitals are shown. If the geometry of the S_1 -state is now slightly distorted in a tetrahedral way due to corresponding normal modes, then orbital $28a''$ will be substantially stabilised, while orbital $30a'$ will be destabilised, in such a way that these two orbitals now become the frontier orbitals and a net stabilisation energy for the whole system is gained. Spin-orbit coupling yields the final triplet state. The reason for this orbital behaviour can be seen from the schematic orbital pictures. While an antibonding interaction in orbital $28a''$ vanishes during the rotation, an antibonding character is introduced into orbital $30a'$ resulting in a completely different frontier orbital structure for the triplet state. As can be seen from orbitals $22a''$ and $38a'$, the elec-

tronic transition to the ground state is now basically of a d-d (LF) type.

The crystal structure of $\text{Pt}(\text{dppb})(\text{CN})_2$ (Figure 3) shows that, in contrast to the isolated molecule, the triplet distortion is hindered by intermolecular steric interactions between the $\text{Pt}(\text{CN})_2$ fragment and two phenyl groups from neighbouring molecules. These groups are oriented perpendicular to the plane spanned by Pt and the two CN groups.

For the complex $\text{Pt}(\text{binap})(\text{CN})_2$, the situation could be different as the binaphthyl substituent is characterised by an extended π -electron system. Accordingly, the lowest-energy transition of binap may not be of the $\text{I} \rightarrow \pi^*$ type but rather a $\pi\pi^*$ transition of the binaphthyl moiety. This assumption is supported by a comparison of the absorption and emission spectra of $\text{Pt}(\text{binap})(\text{CN})_2$ and $\text{Au}_2\text{Cl}_2(\text{binap})$.^[12] For the latter complex it is quite clear that the lowest-energy transitions are of the binap IL type as gold(I) complexes do not have available metal-centred or MLCT excited states at low energies.^[13] Indeed, the long-wavelength region of the absorption spectrum of $\text{Pt}(\text{binap})(\text{CN})_2$ between 270 and 400 nm (Figure 2) is very similar to that of $\text{Au}_2\text{Cl}_2(\text{binap})$. Moreover, the emission spectra of both complexes are also rather similar and resemble the phosphorescence of the free binap ligand which, however, is only observed at low temperatures.^[14] The IL assignment for the phosphorescence of $\text{Pt}(\text{binap})(\text{CN})_2$ is also supported by the fact that the emission shows a pronounced structure which is typical for the phosphorescence from IL states.^[1,15] The phosphorescence of $\text{Pt}(\text{binap})(\text{CN})_2$ appears only in the solid state and is absent in solution. Again, it is suggested that a rigid structure of the solid compound prevents a distortion towards a tetrahedral structure of a low-energy LF state that does not emit in solution.

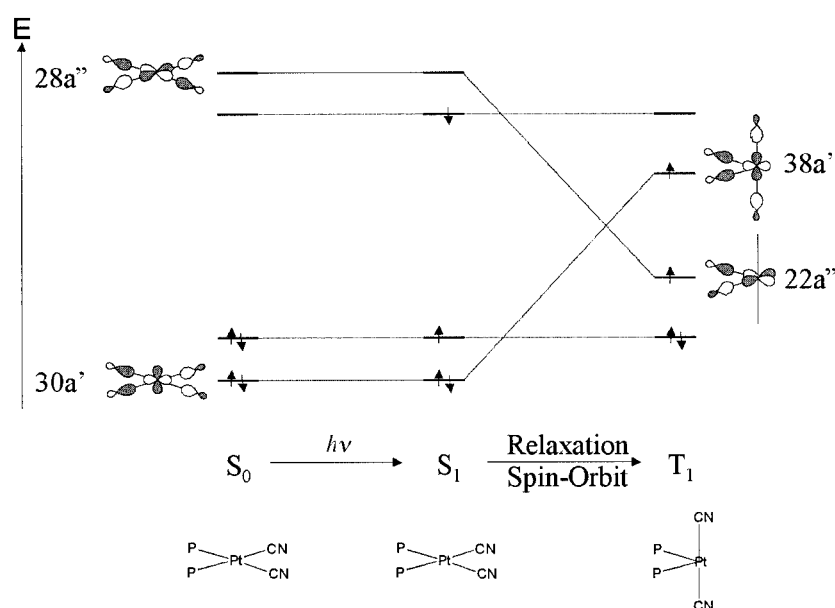


Figure 5. Schematic view of the orbital correlation diagram; only the orbitals responsible for the geometric rearrangement are shown

In summary, solid compounds of the type Pt(P-P)(CN)_2 with bidentate phosphane ligands such as dppb and binap, which carry aromatic chromophores, are triplet emitters under ambient conditions. This phosphorescence originates from MLCT and/or IL states.

Experimental Section

Materials: All solvents used for spectroscopic measurements were of spectrograde quality. Pt(CN)_2 , dppb and binap were commercially available (Aldrich and Strem) and used without further purification. The complexes Pt(P-P)(CN)_2 were obtained by the following procedures.

[Pt(dppb)(CN)₂]: A mixture of Pt(CN)_2 (0.76 g, 3 mmol) and dppb (1.38 g, 3 mmol) in dimethylformamide (70 mL) was refluxed for 6 h. A white powder slowly precipitated. It was collected by filtration, washed with diethyl ether and dried over silica gel under reduced pressure. The resulting white material was purified by recrystallisation from dichloroethane/ether yielding 0.92 g (43%). $\text{C}_{32}\text{H}_{24}\text{N}_2\text{P}_2\text{Pt}$ (693.58): calcd. C 55.42, H 3.49, N 4.04; found C 55.06, H 3.60, N 3.94.

[Pt(binap)(CN)₂] × H₂O: A mixture of Pt(CN)_2 (0.25 g, 1 mmol) and binap (0.63 g, 1 mmol) in dimethylformamide (40 mL) was refluxed for 20 h. After filtration, ether was added to the solution. A slightly yellow powder precipitated. It was collected by filtration, washed with diethyl ether and dried over silica gel under reduced pressure. The resulting slightly yellow material was recrystallised from dichloromethane/ether yielding 0.58 g (65%). $\text{C}_{46}\text{H}_{34}\text{N}_2\text{OP}_2\text{Pt}$ (887.82): calcd. C 62.23, H 3.86, N 3.16; found C 62.68, H 3.90, N 3.07.

X-ray Crystallographic Data for [Pt(dppb)(CN)₂]: $\text{C}_{32}\text{H}_{24}\text{N}_2\text{P}_2\text{Pt}$, $M = 693.6$; $T = 203(2)$ K; monoclinic, $P2_1/n$ (no. 14); $a = 10.031(2)$ Å, $b = 14.885(7)$ Å, $c = 18.812(5)$ Å, $\beta = 98.138(5)^\circ$; $V = 2781(2)$ Å³; $Z = 4$; Data from 2817 reflections, 2626 unique [$R(\text{int.}) = 0.047$], were collected with a Siemens P4 diffractometer by use of $\text{Cu-K}\alpha$ radiation. The structure was refined by full-matrix least-squares refinement with the SHELXL-97 programmes. All non-H atoms were refined anisotropically, hydrogen atoms were included in riding mode with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ to give $R1 = 0.051$, $wR2 = 0.137$ [$I > 2\sigma(I)$] and $R1 = 0.067$, $wR2 = 0.146$ (all data).

CCDC-226785 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Instrumentation: Absorption spectra were measured with a Shimadzu 2100 spectrophotometer. Emission spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The mass spectra were obtained using a TSQ 7000 Finnigan Thermoquest mass spectrometer.

Calculations: Geometries and energies were calculated with the use of density functional theory involving the BP86 functional,^[16] in

combination with a split-valence basis set with polarisation functions on all heavy atoms [SV(P)].^[17] For platinum, an effective core potential with relativistic corrections (ecp-60-mwb; derived from a multielectron fit to the quasi-relativistic Wood–Boring total valence energies) was employed.^[18] The corresponding valence part was of SVP quality.^[19,20] Triplet states were optimised with the unrestricted KS approach. Resolution of identity techniques^[19] was used throughout. All calculations were carried out with the TURBOMOLE software package.^[21]

The orbital correlation diagram is based on the assumption that the relevant excitations are sufficiently described by one-electron transitions between orbitals. We performed additional TD-DFT calculations using the same functional and basis set as described above to check for the single excitation character of the corresponding transitions. The weight of the leading configuration amounts to more than 80% for all relevant singlet excitations. This is also true in the case of the lowest triplet excitation based on the same singlet ground state orbitals for nondistorted geometries. For the distorted triplet geometry the UKS orbitals closely resemble the corresponding RKS orbitals. Therefore the one-electron interpretation is justified.

Acknowledgments

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